# ?-QUALITY MODEL FOR SEN??CA RIVER, ?

By Raymond P. Canale,[1] Emmet M. Owens,[2] Associate Member, ASCE, Martin T. Auer,[3] Associate Member, ASCE, and Steven W. Effler[4]

**ABSTRACT:** The validation of a water-quality model for the Seneca River, a deep, stratifying, slow-moving river located in central New York, is documented. Model validation is supported by comprehensive field monitoring and kinetic experiment programs, and a mass-transport model. The river is severely impacted by the inflow from ionically polluted hypereutrophic Onondaga Lake. Chemical-based density stratification is induced in the river, and attended by violations of dissolved oxygen (DO) and free ammonia standards in the lower layer of the river. The model performed well in matching DO depletions in the lower layer of the river, and diurnal variations in DO. Model projections demonstrate DO standards can only be met by eliminating chemical stratification in the river. The water-quality model is to be used to support regional planning of domestic waste treatment and disposal, including diversion of a major discharge to the river.

## INTRODUCTION

Mathematical models have gained wide acceptance as invaluable tools to support the effective management of impacted rivers and lakes (Thomann and Mueller 1987). Mass-balance models for dissolved oxygen (DO) have long been important tools in engineering analysis of stream and river water quality (Streeter and Phelps 1925); they are routinely applied for river waste-load allocation (Bowie et al. 1985; Krenkel and Novotny 1979; Thomann and Mueller 1987). Mass-balance models have been successfully developed for many other constituents of water-quality concern in recent years [e.g., Chapra and Reckhow (1983) and Thomann and Mueller (1987)].

Model credibility must be established to support expensive water-quality management decisions. Most often this is accomplished through model calibration, a process in which simulations are made to match observations through the "tuning" of model coefficients within acceptable bounds established in the literature [e.g., Bowie et al. (1985)]. Model verification, the demonstration of model fit for a distinctly different set of environmental conditions, with the same suite of coefficients used in calibration, establishes a much enhanced level of credibility. However, the opportunity for verification does not always exist (e.g., narrow range of water quality conditions prevails), thereby eliminating the practical testing of a calibrated model and the coefficient values established through the calibration process. Alternatively, model credibility can be enhanced through the system-specific determination of model coefficients. A model is said to be validated in cases in which all inputs and kinetic coefficients are independently measured and simulations match observations.

Here we document the development and validation of a water-quality model for dissolved oxygen for a hydrodynamically complex river system that is impacted by an adjoining polluted lake. The validated model is used to evaluate the processes contributing to prevailing violations of water-quality standards, and to demonstrate the need to eliminate pollution-based stratified flow in the river to meet standards. The model is to be used to support regional planning of domestic waste treatment and disposal. Specifically, various management alternatives aimed at restoring the water quality of the adjoining lake, including diversion of a major domestic waste discharge to the river system, are to be evaluated with respect to the acceptability of their impact on the river system.

## DESCRIPTION OF SYSTEM

### Seneca River and Three Rivers System

The Seneca River is part of the Three Rivers system, which drains more than 13,000 km$^2$ in central New York state to Lake Ontario. A schematic of the eastern portion of the river, and its position within the Three Rivers system, is presented in Fig. 1(a). The Seneca River is highly turbid and eutrophic downstream of Cross Lake; e.g., related summer average conditions measured at Baldwinsville in 1990 were Secchi disk transparency of 0.75 m, total phosphorus concentration of 70 $\mu g \cdot L^{-1}$, and chlorophyll concentration of 34 $\mu g \cdot L^{-1}$. The Seneca and Oneida Rivers combine at the Three Rivers Junctions, 3.0 km upstream of Phoenix [Fig. 1(a)], to form the Oswego River. The Oswego River is the second-largest fluvial discharge (following the Niagara River) to Lake Ontario.

The natural water-flow and mass-transport characteristics of this river system have been greatly altered [e.g., dams and locks, Fig. 1(a)] to support navigation and hydroelectric power generation. The Three Rivers system is an integral part of the New York State Barge Canal System. The bounding three eutrophic lakes [e.g., Effler et al. (1984, 1989)], Cross, Onondaga, and Oneida Lakes, play prominent roles in regulating the water quality of the river system. All three of the rivers have a New York state water-quality classification of B. The river system is used for waste disposal, as well as fishing and navigation. There are presently nine point-source discharges to the Seneca and Oswego Rivers over the limits of Fig. 1(a), including two breweries. Three of the discharges enter the Seneca River. This region of New York has been attractive to industries because of the availability of surface waters for economical waste disposal (Calocerinos & Spina 1984). The permitted discharges presently allowed for this reach of the Seneca River are 0.81 $m^3 \cdot s^{-1}$ of flow, 4,870 $kg \cdot d^{-1}$ of nitrogenous oxygen demand, and 4,095 $kg \cdot d^{-1}$ of carbonaceous oxygen demand.

The principal focus of this study is the reach from downstream of the Baldwinsville dam on the Seneca River to the Phoenix dam [Fig. 1(b)]. This is the most degraded portion of the Three Rivers System and it may be most affected by remediation measures for Onondaga Lake.

[1]Prof., Dept. of Civ. and Envir. Engrg., Univ. Michigan, Ann Arbor, MI 48109.

[2]Asst. Prof., Dept. of Civ. and Envir. Engrg., Syracuse Univ., Syracuse, NY 13244.

[3]Prof., Dept. of Civ. and Envir. Engrg., Michigan Tech. Univ., Houghton, MI 49931.

[4]Res. Engr., Upstate Freshwater Inst., P.O. Box 506, Syracuse, NY 13214.

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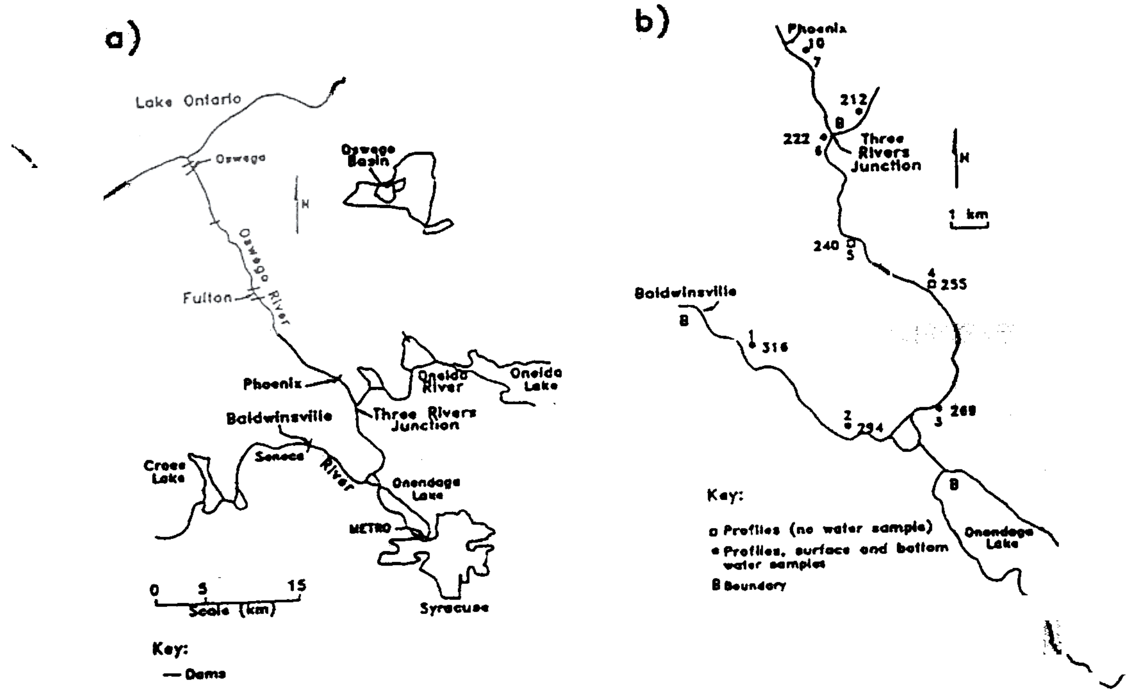


FIG. 1. (a) Three Rivers System; (b) Study Section, with Sampling and Experiment Locations

## Onondaga Lake

The existing degradation of the river is largely a manifestation of the input of pollutants from Onondaga Lake (Effler et al. 1984). Onondaga Lake has been described as the most polluted in the United States (U.S. Senate 1989). Onondaga Lake is bordered by the city of Syracuse [Fig. 1(a)], the largest population center in the Three Rivers basin. The lake has received most of the wastewater from the metropolitan area since the development of the region. The lake is polluted with phosphorus (Canale and Effler 1989) and ammonia [T-$NH_3$; Effler et al. (1990)], due largely to loadings from the Metropolitan Sewage Treatment Plant (METRO), located at the southern end of the lake [Fig. 1(a)]. METRO (average discharge of about 3.1 $m^3 \cdot s^{-1}$) contributes approximately 19% of the flow to the lake on an annual basis, but as much as 45% during the summer months (Effler et al. 1990). Manifestations of hypereutrophy result in contraventions of state standards for clarity (Auer et al. 1990) and dissolved oxygen (Effler et al. 1988) in the lake. Standards for free ammonia ($NH_3$) to protect nonsalmonid fish are violated at all depths in the lake for most of the summer; margins of contraventions are particularly great in the upper waters (Effler et al. 1990). A leading remediation alternative for the lake presently under consideration includes diversion of a portion, or all, of the METRO effluent to the Seneca River.

The lake is also ionically polluted [mostly chloride ($Cl^-$), sodium, and calcium] as a result of waste discharges from a Solvay process soda ash facility on the western shore of the lake [e.g., Effler (1987) and Effler and Driscoll (1985)]. The ionic enrichment elevates the density of the lake water (Effler et al. 1986). The average chloride concentration of the lake was about 1,600 $mg \cdot L^{-1}$ before closure of the facility in 1986 (Doerr et al. 1994). However, the lake remains ionically enriched [e.g., average $Cl^-$ concentration of 430 $mg \cdot L^{-1}$ for 1990 and 1991 (Doerr et al. (1994)], in part because of continuing discharges from a waste-bed area (Effler et al. 1991).

The natural hydraulic gradient that existed between Onondaga Lake and the Seneca River was eliminated through a combination of the lowering of the lake (1.2 m in 1822) and modifications to the river to support navigation. This, together with the elevated density of the lake compared to the Seneca River (Effler et al. 1984), causes an unusual bidirectional flow regime to prevail in the lake outlet. Relatively dense lake-surface water exits along the bottom of the outlet to the river and river water flows into the lake in the top of the outlet channel (Owens and Effler 1994).

## Stratification and Water Quality in Seneca River

During periods of low flow, stratified flow exists in both the lake outlet and adjacent portions of the Seneca River. Features of the stratification phenomenon in the river documented in 1991, including vertical structure, longitudinal extent, effect of river flow on magnitude of stratification, and water-quality implications, are illustrated in Fig. 2(a–c). The vertical profile of specific conductance measured on July 30, 1991 at a station [No. 5, Fig. 1(b)] 8.1 km downstream from the point of entry of Onondaga Lake clearly depicts chemical stratification in the river. The negative implications of the stratification phenomenon for the river's oxygen resources are apparent from the paired oxygen profile [Fig. 2(a)]; oxygen is greatly depleted in the lower stratified layer. This represents a violation of the minimum DO standard (4.0 $mg \cdot L^{-1}$) for class B (as well as other classes) waters in New York State. The oxygen depletion in the stratified layer has been attributed to the isolation of the lower layer (containing the Onondaga Lake outflow) from the oxygen sources of reaeration and photosynthesis, combined with the continued exertion of oxygen consuming processes (Effler et al. 1984).

The longitudinal profiles for the upper (0.5 m below the surface) and lower (0.5 m above the river bottom) waters presented for July 30, 1991 in Fig. 2(b) illustrate the longitudinal extent of the stratification phenomenon and related water-quality problems during low-flow periods. Here vertical differences in $Cl^-$ concentration reflect chemical stratification. Note that the stratification extends upstream as well as downstream from the point of entry of Onondaga Lake. The upstream movement, or "salt wedge" effect, is commonly observed in stratified estuaries (Thomann and Mueller 1987).

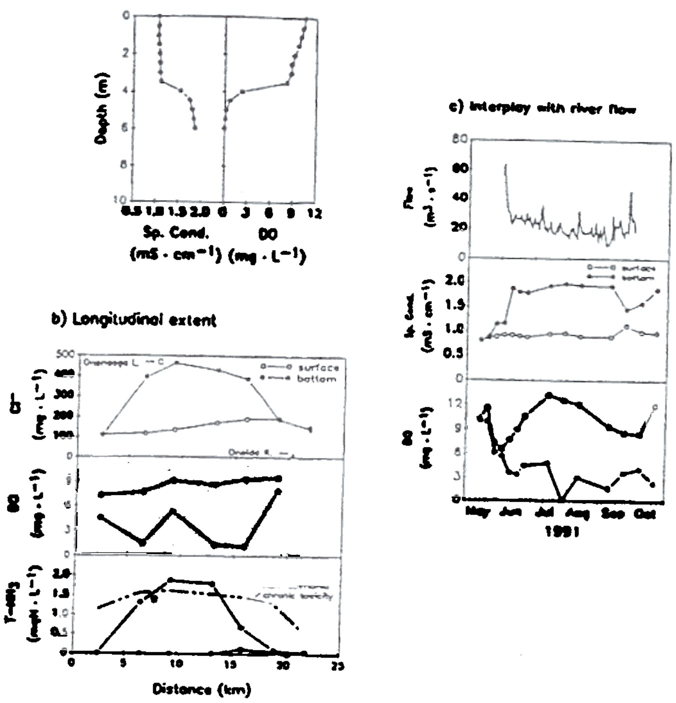


FIG. 2. Prevailing Seneca River Conditions: (a) Stratification for Specific Conductance and Dissolved Oxygen, July 30, 1991; (b) Longitudinal Extent of Stratification and Violations of DO and $NH_3$ Standards, July 30, 1991; and (c) Interplay of Stratification and DO Violations with River Flow

but is unique for inland rivers. The concentration of $Cl^-$, a conservative substance, increases in the upper waters and decreases in the lower waters progressively downstream of the lake inflow as a result of vertical mixing. On July 30, 1991 the stratification extended more than 8 km downstream of the lake. The chemical stratification promotes the extension of Onondaga Lake's problems into the Seneca River. Strong DO depletion occurs in the lower layer of the river upstream, as well as downstream, of the point of entry of the lake, causing violations of the DO standard in both sections of the river [Fig. 2(b)]. The high T-$NH_3$ concentrations retained in the lower layers adjoining the inflow of the lake, and the attendant pH and temperature conditions (not shown), cause violations of the state's $NH_3$ standard [Fig. 2(b)]. The extent of stratification and related impact on oxygen resources of the river was greater before closure of the soda ash facility (Effler et al. 1984). In low-flow periods during the operation of the facility, the stratification persisted 14 km downstream to the dam in Phoenix. Presently the stratification is broken up before the confluence with the Oneida River [Fig. 1(b)].

The occurrence of stratification, and the coupled depletion of DO in the lower layer, is limited to periods of low river flow, as illustrated for a downstream site [No. 4, Fig. 1(b)] in Fig. 2(c). A critical flow for this site appears to be about 80 $m^3 \cdot s^{-1}$ [Fig. 2(c)]; above this flow the turbulence is great enough to break up the stratification. The critical flow is somewhat higher closer to the entry point of Onondaga Lake. Stratification prevailed at site No. 4 for at least 5 months in 1991, and violations (e.g., <4 $mg \cdot L^{-1}$) of the DO standard occurred in the lower layer on about 60% of the days over the June–October interval. Substantial year-to-year variations in the duration of stratification and the occurrences of coupled water-quality violations doubtless occur in the river as a result of the large annual variations in river flow that are common to this region. The conditions presented for 1991 in Fig. 2(c) probably approach worst case (with respect to duration) for the present water quality of Onondaga Lake, because the flow at Baldwinsville was less than the 30Q10 value (17.6 $m^3 \cdot s^{-1}$) for a substantial portion of the summer.

## WATER-QUALITY MODEL

### Model Framework

The water-quality model uses a multiple-box or multiple-segment approach [e.g., Shanahan and Harleman (1984)]. The river is divided into a number of segments; the concentrations within each segment are assumed to be uniform. The generalized mass balance expression for DO in each segment in the river is

accumulation = reaeration + [photosynthesis (P)

− respiration (R)] − oxidation of CBOD

− oxidation of NBOD − sediment oxygen demand

+ oxygen inputs ± oxygen transport (1)

where CBOD = carbonaceous biochemical oxygen demand; and NBOD = nitrogenous biochemical oxygen demand. Sources of DO include reaeration, photosynthesis (net; i.e., gross photosynthesis minus respiration), inputs from tributaries or effluents, and oxygen transported into segment $i$ from adjoining segments. Oxygen sinks include oxidation of carbonaceous material, oxidation of nitrogenous material (nitrification), oxygen demand exerted by sediments at the interface, and oxygen transported out of segment $i$ to adjoining segments. The kinetic expressions are presented next, in a format consistent with (1)

$$V_i(dC_i/dt) = [k_a\cdot(C_s - C_i) + (P_g - R)\cdot \mathrm{Chl}_i - k_c\cdot \mathrm{CBOD}_u - k_n\cdot \mathrm{NBOD}_u - \mathrm{SOD}/H]\cdot V_i + \text{oxygen inputs} + Q_{ij}(C_j - C_i) + E_{ij}(A_{ij}/l_{ij})(C_j - C_i) \quad (2)$$

where $V_i$ = volume of model segment $i$ ($m^3$); $C_i$ = concentration of DO in segment $i$ ($mg \cdot L^{-1}$); $t$ = time (d); $C_s$ = DO concentration at saturation ($mg \cdot L^{-1}$); $P_g$ = gross photosynthesis ($mg\ O_2 \cdot \mu g$ chlorophyll$^{-1} \cdot d^{-1}$); $R$ = plant respiration ($mg\ O_2 \cdot \mu g$ chlorophyll$^{-1} \cdot d^{-1}$); $\mathrm{Chl}_i$ = concentration of chlorophyll in segment $i$ ($\mu g \cdot L^{-1}$); $k_a$, $k_c$, $k_n$ = rate coefficients for reaeration and carbonaceous and nitrogenous BOD decay ($d^{-1}$); $\mathrm{CBOD}_u$ = concentration of ultimate CBOD ($mg \cdot L^{-1}$); $\mathrm{NBOD}_u$ = concentration of ultimate NBOD ($mg \cdot L^{-1}$); SOD = sediment oxygen demand ($mg\ O_2 \cdot m^{-2} \cdot d^{-1}$); $H$ = depth (m); $Q_{ij}$ = flow from adjoining segment $j$ to segment $i$ ($m^3 \cdot d^{-1}$); $E_{ij}$ = diffusion/dispersion coefficient at interface between segment $j$ and $i$ ($m^2 \cdot d^{-1}$); $A_{ij}$ = area of interface between segment $j$ and $i$ ($m^2$); and $l_{ij}$ = distance between segment $j$ and $i$ (m). Temperature adjustments for the kinetic processes were made according to the Arrhenius format

$$k_{x,T} = k_{x,20}\cdot\Theta^{T-20} \quad (3)$$

where $k_{x,T}$ and $k_{x,20}$ = values of kinetic coefficient $x$ at tem-

TABLE 1. Values of Θ for Seneca River Oxygen Model Kinetic Coefficients

| Coefficient (1) | Θ (2) |
|---|---|
| $k_a$ | |
| $P_g$ | |
| $R$ | |
| $k_c$ | |
| $k_n$ | |
| SOD | |

peratures $T$ and 20°C; and $\Theta$ = d[illegible]ss temperature coefficient. The values of $\Theta$ for the [illegible] coefficients appear in Table 1.

Similar mass-balance approaches were utilized to simulate $CBOD_u$ in a submodel of the oxygen model. The mass-transport processes in this complex system are determined separately with a calibrated transport submodel (described subsequently); outputs from this submodel serve as inputs for the biochemical models. The range in diurnal variation in DO, driven by plant metabolism, and modulated by reaeration, was estimated from predictions of a phytoplankton production submodel (described subsequently) and determinations of $k_a$ according to a modified formulation of the "delta" method that accounts for stratification (Chapra and DiToro 1991).

## Monitoring Program

An intensive program of field measurements, sampling and laboratory analyses was conducted in 1990 and 1991 to support the development, testing, and application of the water quality model. The goals were to: (1) Characterize the prevailing water quality in the river system; (2) develop an understanding of the processes that regulate these conditions; and (3) document environmental forcing and system boundary conditions. The design of the monitoring program (Table 2) was guided by the findings of earlier studies of the system [e.g., Calocerinos & Spina (1984), Effler (1982), and Effler et al. (1984)] and the needs of the water-quality model [(2)].

Sampling stations for the monitoring program are shown in Fig. 1(b), along with buoy numbers. Seven sites were positioned along the study reach. These stations, and a site near the mouth of th[illegible] River that establishes boundary conditions for this inflow, were monitored routinely over the May–October interval of 1990 and 1991. The very important boundary conditions of the Onondaga Lake inflow are established through an ongoing comprehensive monitoring program [e.g., Effler et al. (1988, 1990) and Onondaga County (1971–1990)]. The river stations were monitored weekly in 1990, and in May and June of 1991; monitoring was conducted biweekly over the July–October interval of 1991. In-situ profile measurements of DO, temperature, specific conductance, and pH were made (Table 2) at all stations to assess the occurrence and character of stratification. Profiles of underwater irradiance, to support determination of the attenuation coefficient for downwelling irradiance ($k_d$, $m^{-1}$), were collected routinely at site No. 2 [Fig. 1(b)] in 1991 and irregularly at all the stations in 1990. Samples for laboratory analyses were collected routinely from two depths (Table 2) at each station.

Additionally, in-situ diurnal measurements of DO, temperature, pH, and specific conductance were made at two depths on five dates over the July–September interval of 1991. Each station was usually visited eight times (e.g., 3-hr return frequency) within a 24-hr period. These measurements supported calculations of daily average conditions, as well as established the range of DO concentrations within a day to support testing of the water quality model. Concentrations of sulfur hexafluoride ($SF_6$) were measured in samples collected at the routine monitoring sites of Fig. 1(b) and below the Phoenix dam over the interval of the last three diurnal surveys of 1991 to support estimates of $k_a$ (see subsequent treatment).

TABLE 2. Monitoring Program for Seneca River, 1990 and 1991

| Parameters (1) | Depths (2) | Comments/justification (3) |
|---|---|---|
| Lab | | |
| $CBOD_5$[a] | 0.5 m below surface/0.5 m above bottom | oxygen sink, $CBOD_u$[a] in model |
| T-$NH_3$,[b] $NO_3$ + $NO_2$ | | toxicity status, nitrification, nutrients |
| Cl | | conservative, hydrodynamic tracer, modeled parameter |
| Turbidity | | light attenuation |
| TP[c] | | trophic state |
| Chlorophyll | | trophic state, *P/R* submodel |
| SRP[d] | | nutrient, *P/R* submodel |
| $SF_6$[e] | | inert insoluble tracer gas, support determination of $k_a$ |
| Field | | |
| DO | 0.5 m intervals | modeled parameter, water-quality status |
| Temperature | 0.5 m intervals | DO% saturation, stratification, ammonia toxicity |
| Specific conductance | 0.5 m intervals | stratification, measure of salinity (conservative) |
| pH | 0.5 m intervals | ammonia toxicity |
| Underwater irradiance | 0.25 m intervals | calculation of light attenuation coefficient [$k_d$, $m^{-1}$; e.g., Effler et al. (1991b)], *P/R* submodel |
| Secchi disk | | light attenuation, water quality |
| Incident irradiance | | hourly integrated, continuously measured, *P/R* submodel |
| Flow[f] | | transport submodel |

[a]Carbonaceous biochemical oxygen demand on filtered (0.45 μm) samples, inhibited for nitrification; ultimate CBOD ($CBOD_u$) = 1.3·$CBOD_5$.
[b]Total ammonia.
[c]Total phosphorus.
[d]Soluble reactive phosphorus.
[e]Sulfur hexafluoride.
[f]Location of gauges shown in Fig. 1(a).

## Transport Submodel

A mass-transport submodel was developed to simulate the complex flow and transport patterns that exist in this river system. This transport submodel defined the array of linked segments to which a mass balance equation of the form of Eq. (2) was applied, and defined the interaction of adjacent segments through the processes of horizontal and vertical advection, longitudinal dispersion, and vertical diffusion. Details of the development of the mass transport submodel, and its application in the estimation of the reaeration coefficient, are described by Naumann (1993). The magnitude of the individual processes in the mass transport submodel were determined independently of the water-quality model through simulations of a conservative constituent (salinity). The transport model is not entirely predictive in that certain components of the submodel are based on observations from the monitoring program. However, the water-quality model was applied to flow and transport conditions that differ only slightly from 1991 conditions.

The most important feature of the mass-transport submodel with regard to the unusual water-quality conditions in the Seneca River is its use of two layers to describe the stratified conditions. As shown in Fig. 2, the vertical profiles of specific conductance, dissolved oxygen, and other physical and chemical parameters may be approximated by two completely mixed layers. The use of a layered approach is very unusual in a water quality model of a nonestuarine river, but is critical for the simulation of the stratified conditions. The surface and bottom layers are then further divided into an array of longitudinal segments.

Features of the transport submodel and its application to the Seneca River are presented in Fig. 3, including: (1) Morphometric characteristics [Fig. 3(a)]; (2) description of the flow pattern in the river proximate to the inflow of Onondaga Lake [Fig. 3(b)]; (3) longitudinal and vertical

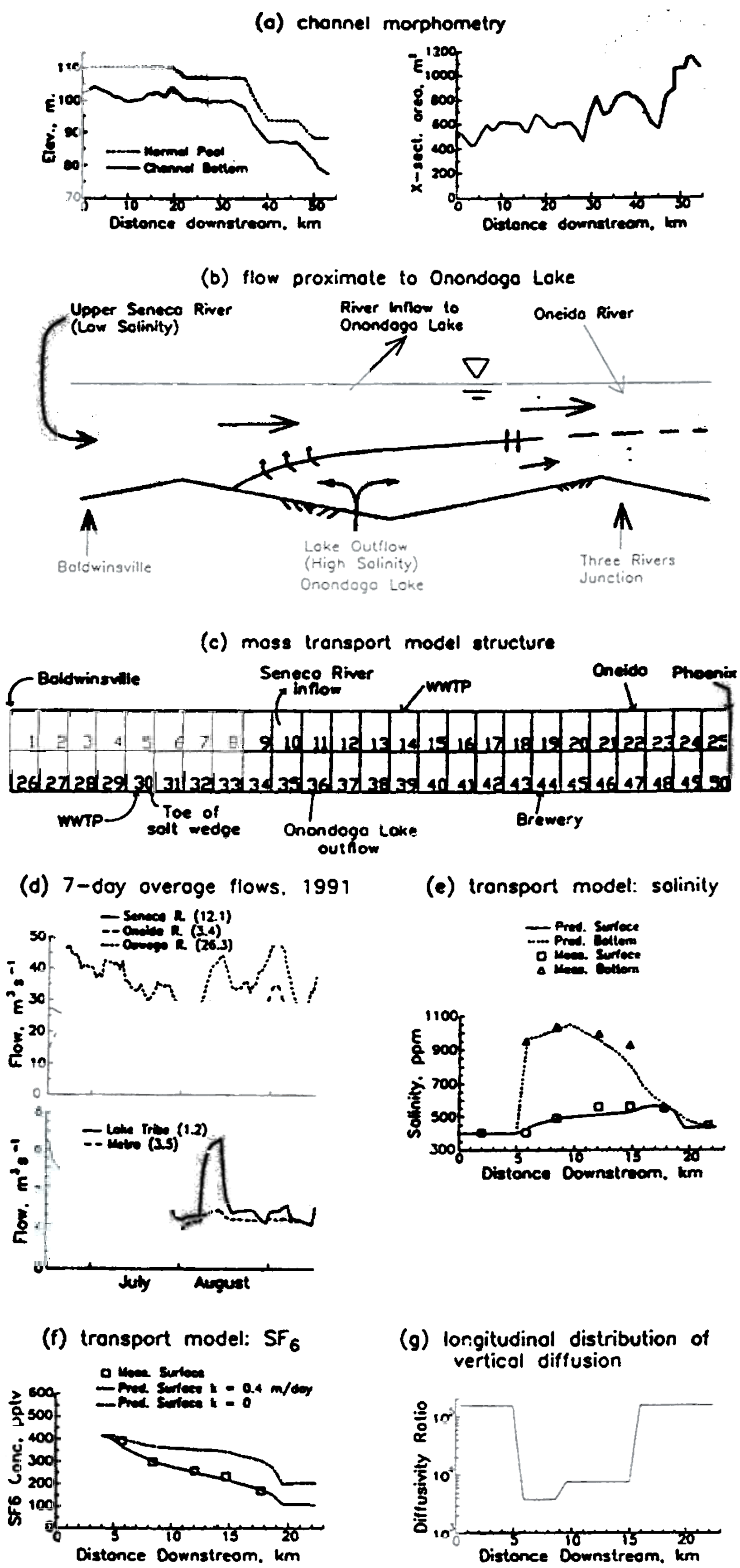


FIG. 3. Transport Submodel: (a) River Morphometry; (b) Flow Pattern Proximate to Onondaga Lake Inflow; (c) Model Framework; (d) River and Lake Flows, 7-Day Average; (e) Calibration of Transport Model; (f) Application of Transport Model to $SF_6$ Experiments; and (g) Distribution of Vertical Dispersion Coefficient Values along Study Reach

segmentation of the transport (and [illegible] lity) model [Fig. 3(c)]; (4) temporal distributions of [illegible] inflows for the study period [Fig. 3(d)]; (5) calibration of the transport model for the third diurnal survey (July 29–30, 1991) [Fig. 3(e)]; (6) application to support estimate of the $SF_6$ mass-transfer coefficient [Fig. 3(f)]; and (7) longitudinal distribution of the vertical turbulent diffusion coefficient [$E_{ij}$; $m^2 \cdot d^{-1}$; Fig. 3(g)].

The Baldwinsville to Phoenix study reach was partitioned into 25 longitudinal segments of about 0.9 km length [Fig. 3(c)]. The interface between the upper and lower layers was placed at the location of maximum vertical gradient in salinity as determined from measurements; the average depth to this interface was 3 m. The geometries of the 50 transport-model segments were determined from river channel morphometric data [O'Brien & Gere Engineers (1977); Fig. 3(a)]. For low-flow conditions, such as those experienced in 1991 [Fig. 3(d)], the volumes of the model segments are constant, due to small variations in water-surface elevation. Equal velocities of flow are assumed for the two layers upstream of the "salt wedge," the stratified region upstream of the lake outflow [Fig. 3(b and c)]. The magnitude of the "salt wedge" flow (Arita and Jirka 1987) was determined as part of the calibration of the transport model. The flow in the bottom layer immediately downstream of the lake is water that has flowed from Onondaga Lake. Five inflows that are significant in terms of either discharge or pollutant loading were included in the Baldwinsville-Phoenix reach, the Onondaga Lake outflow, flow from the Oneida River, and inputs from three wastewater-treatment plants (WWTP). The Oneida River was assumed to enter the surface layer, while the entry of the three WWTP discharges was based on the outfall elevations.

River and Onondaga Lake tributary flows were low during the summer of 1991 [Fig. 3(d)]. Though flows in the Seneca River were less than the 30Q10 (17.6 $m^3 \cdot s^{-1}$) for portions of the study period, they remained above the 7Q10 of 12.1 $m^3 \cdot s^{-1}$. Note that the inflow from METRO to the lake represented nearly 50% of the total at times in 1991. The value of the longitudinal dispersion coefficient determined for the Seneca River from an instantaneous dye release during low flow conditions in September of 1991 was $1.5 \times 10^6$ $m^2 \cdot d^{-1}$.

The transport submodel was calibrated to salinity for the purpose of determining the magnitude of vertical turbulent diffusion between the two layers over the reach from Baldwinsville to Phoenix. The simulated and measured salinity in the two layers for the July 29–30, 1991 survey is shown in Fig. 3(e). The lowest vertical diffusion occurs in the "salt wedge" region, while the highest occurs outside the region of salinity stratification. The application of the model to salinity is described in detail by Naumann (1993). The segment geometric properties [$V_i$, $A_{ij}$, and $l_{ij}$ in (2)] and the longitudinal dispersion coefficient [$E_{ij}$ in (2) for adjacent segments in the same layer] were held constant for all simulations. The vertical diffusion coefficient ($E_{ij}$ for adjacent segments in different layers) was varied during model validation runs based on salinity simulations. Advection [$Q_{ij}$ in (2)] was varied based on the inflows to the system.

Following this calibration procedure, the transport submodel was applied to the dissolved gas $SF_6$ [Fig. 3(f)], which was deliberately injected into the river flow at Baldwinsville for a portion of the study period. The application of the submodel to $SF_6$ is described in detail by Naumann (1993), and is summarized in the next section. The same transport submodel was also applied to simulate each of the mass constituents in the water-quality model, using the magnitude of the transport processes determined from calibration to the observed salinity distributions.

## Development of [illegible] Coefficients

A summary of the development of the kinetic coefficients for the river-water-quality model is presented as Table 3. Additional descriptive information is provided in this section.

SOD: The distribution of SOD along the study reach was established (Fig. 4) through a combination of field and laboratory studies. Portions of the reach have little or no sediment deposits and thus SOD is not exerted in these sections. The profile of SOD was based on COD analyses of sediment samples collected at eight locations over the longitudinal extent of sediment occurrence [Fig. 1(b)], based on the empirical relationship developed by Gardiner et al. [(1984) Table 3]. This relationship was supported for the river system by direct determination of SOD on two intact core samples (Fig. 4), using the Gardiner et al. (1984) methodology. A SOD profile consistent with the model segmentation was developed by interpolation.

$k_n$: A number of researchers have reported nitrification to be localized at the sediment-water interface (Cavari 1977; Curtis et al. 1975; Hall 1986). Results of our laboratory microcosm experiments are consistent with these observations and indicate no significant nitrification occurs within the water column of the Seneca River. The kinetics of nitrification in the river were therefore quantified based on sediment flux of $T\text{-}NH_3$ (depletion) determined in laboratory experiments with intact sediment cores. These results were represented in first-order kinetic form [(2)] by utilizing a film theory approach, as described in Table 3, analogous to reaeration [e.g., Bowie et al. (1985)]. This treatment assumes that diffusion-based transport of $T\text{-}NH_3$ from the overlying bulk liquid across the stagnant fluid layer (film) immediately overlying the sediments (nitrifying bacteria) is the rate-limiting step for nitrification. The film-transfer coefficient [$K_f$, in Table 3] for nitrification was found to be in the range of 0.08 to 0.33 $m \cdot d^{-1}$. A model value of 0.135 $m \cdot d^{-1}$ was selected from this range by comparison with observed $T\text{-}NH_3$ profiles in the river. The corresponding value of $k_n$ was estimated to be 0.021 $d^{-1}$ (for an average river depth of 6.4 m). This value is lower than many reported for other streams and rivers, but generally consistent with the observation that lower values are associated with deeper systems. According to Table 3, lower values of $k_n$ are expected as $H$ increases.

$k_c$: It's important to differentiate among the oxygen sinks of decay of CBOD, phytoplankton respiration, and the process of nitrification. Thus, the estimation of $k_c$ was based on laboratory BOD analyses of filtered (0.45 μm) nitrification-inhibited samples. Samples represented a realistic mixture of METRO (one part) and the Seneca River (four parts) under critical low flow conditions for an Onondaga Lake management option of full diversion of METRO to the river. A value of $k_c = 0.11$ $d^{-1}$ was determined, using the Thomas slope method (Metcalf and Eddy 1979). A nearly equivalent value (0.1 $d^{-1}$) was estimated for present conditions, based on calibration of the CBOD submodel against $CBOD_u$ profiles measured in the river.

$k_a$: Direct experimental determination of $k_a$ was deemed necessary because of the substantial uncertainty of estimates based on empirical expressions for rivers of this great depth and low velocity of flow [e.g., Bowie et al. (1985)], and the absence of a clearly defined DO "sag" in the surface waters that could support estimates through model calibration. The inert, relatively insoluble gas $SF_6$ was continuously injected at Baldwinsville for several weeks during the study period, and its concentration in the water was measured periodically at points downstream. The gas $SF_6$ was selected over the more widely used propane for this large river because of its much lower analytical detection limits. Wanninkhof et al. (1987, TA

| Coefficient (1) | Components/description (2) | Reference (3) |
|---|---|---|
| SOD | field survey to establish the distribution of river deposits | |
| | SOD determinations (2) on intact core samples [Fig. 1(b)] | Gardiner et al. (1984) |
| | COD river sediment profile [$n$ = 10; Fig. 1(b)] | |
| | SOD river profile from COD profile, according to SOD = (7.66·COD)/(157 + COD) | Gardiner et al. (1984) |
| $k_n$ | determination of T-NH$_3$ flux ($J$; mg·m$^{-2}$·d$^{-1}$) on intact core samples (3) | |
| | determination of film transfer coefficient ($K_f$; m·d$^{-1}$), $K_f$ = $J$/[T-NH$_3$]; where [T-NH$_3$] = bulk concentration of T-NH$_3$ (mg·L$^{-1}$) | |
| | determination of first-order nitrification rate constant ($k_n$; d$^{-1}$); $k_n$ = $K_f/H_l$; where $H_l$ = river depth of lower layer (m) | |
| $k_r$ | laboratory BOD analyses; filtered (0.45 μm) and nitrification inhibited; DO monitored daily | APHA (1985) |
| | $K_r$ determined from results according to Thomas slope method | Metcalf & Eddy Inc. (1979) |
| | calibration of field measurements | |
| $k_a$ | continuous injection of SF$_6$ downstream of Baldwinsville [Fig. 1(b)] for 5 weeks | |
| | downstream monitoring of SF$_6$ | Wanninkhof et al. (1987) |
| | oxygen transfer coefficient ($K_L$; m·d$^{-1}$) determined from SF$_6$ exchange coefficient ($K_{SF}$; m·d$^{-1}$): $K_L$ = 1.38·$K_{SF}$ | |
| | reaeration coefficient ($k_a$; d$^{-1}$) for upper cells of river model; $k_a$ = $K_L/H_u$; where $H_u$ = depth of upper layer (m) | |
| $P/R$ | laboratory measurements of gross photosynthesis and respiration with Seneca River phytoplankton to develop productivity irradiance ($P$-$I$) curve | Storey et al. (1993a,b) |
| | field verification of $P$-$I$ curve by in-situ light-dark bottle technique | Storey et al. (1993b); Vollenweider (1974); Auer et al. (1986) |
| | chlorophyll-light attenuation relationship for Seneca River; $k_d$ = 0.0056Chl + 1.53; where $k_d$ = light attenuation coefficient and Chl = chlorophyll concentration (μg·L$^{-1}$) | |
| | photosynthesis submodel; accommodates influences of light, temperature, and nutrients | Storey et al. (1993a,b) |
| | calculation of diurnal ranges in DO ("delta") using "delta" method | Chapra and DiToro (1991) |

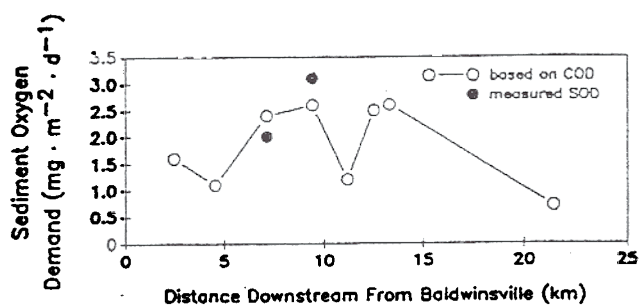


FIG. 4. Longitudinal Distribution of SOD along Study Reach

1990) have documented the successful use of SF$_6$ to assess gas exchange for a range of surface-water systems.

The value of the SF$_6$ surface-mass-transfer coefficient ($K_{SF}$; m·d$^{-1}$) was determined with the mass transport model [e.g., Fig. 3(f)] that had been calibrated for salinity [Fig. 3(e); Naumann (1993)]. The mass-transfer coefficient for oxygen ($K_L$) is determined directly from $K_{SF}$ (Table 3) based on the differences of the molecular-diffusion coefficients for the two gases. Substantial longitudinal differences in $K_{SF}$ were not identified in the experimental results; however, temporal differences were observed during the study period; e.g., the values of $K_L$ determined for the last three model validation surveys were 0.55, 0.90, and 0.55 m·d$^{-1}$, respectively. The values for the first two surveys were estimated, from an empirical $K_{SF}$-flow relationship, to be 0.83 and 0.76 m·d$^{-1}$. Variations in wind conditions probably also contribute to dynamics in $K_L$ for this deep, slow-moving river. The reaeration coefficients ($k_a$) for the upper model cells are calculated directly from the gas-exchange coefficients (Table 3).

*P/R*: The source-sink character of the algal component of the DO mass balance of productive rivers and streams varies among days and changes within days due to natural variation in incident light (Auer and Effler 1989). These influences, as well as the effects of temperature and nutrient availability, were accommodated with the following phytoplankton-production submodel

$$P_n = P_{g.max.20} \cdot \frac{I}{K_I + I} \cdot \frac{\text{SRP}}{K_p + \text{SRP}}\, \Theta_p^{(T-20)} - R_{20}\Theta_R^{(T-20)} \quad (4)$$

where $P_n$ = chlorophyll-specific rate of net photosynthesis (mg O$_2$·μg chlorophyll$^{-1}$·d$^{-1}$); $P_{g.max.20}$ = maximum chlorophyll-specific rate of gross photosynthesis (=0.6 mg O$_2$·μg chlorophyll$^{-1}$·d$^{-1}$) at 20°C; $I$ = irradiance (μE·m$^{-2}$·s$^{-1}$); $K_I$ = half-saturation coefficient for irradiance (=180 μE·m$^{-2}$·s$^{-1}$); $R_{20}$ = chlorophyll-specific respiration rate (=0.04 mg O$_2$·μg chlorophyll$^{-1}$·d$^{-1}$) at 20°C; SRP = concentration of soluble reactive phosphorus (μg·L$^{-1}$), $K_p$ = half-saturation coefficient for SRP (μg·L$^{-1}$); $\Theta_p$ = dimensionless temperature coefficient for photosynthesis; and $\Theta_R$ = dimensionless temperature coefficient for respiration.

Kinetic coefficients describing the photosynthesis-light relationship [$P$-$I$ curve; e.g., Auer and Effler (1990a)] were determined through laboratory experiments with the natural phytoplankton assemblage of the river (Table 3) and verified by field incubations at several depths in the river (Storey et al. 1993b). Site-specific determination of these coefficients enhances model credibility (Auer and Canale 1986; Storey et al. 1993a). Light and photosynthesis were integrated over both time (hourly) and depth (0.25-m depth intervals) to support accurate calculations [e.g., Auer and Effler (1990b)]. Values of $k_d$ for sites without direct measurements were estimated from values of Chl, according to a system-specific empirical relationship (Table 3), based on the subset of paired observations. The large background attenuation [1.53 m$^{-1}$, Table 3] reflects the high nonalgal turbidity of the river, a situation that is common to many large rivers.

## MODEL PERFORMANCE AND APPLICATION

### Validation of Model

Simulations of the water-quality model are compared to observations in Fig. 5(a–c). Model predictions in general closely match measurements. Comparisons are shown here for one of the diurnal surveys of 1991 for CBOD, representative of conditions and model performance for all five surveys. Note

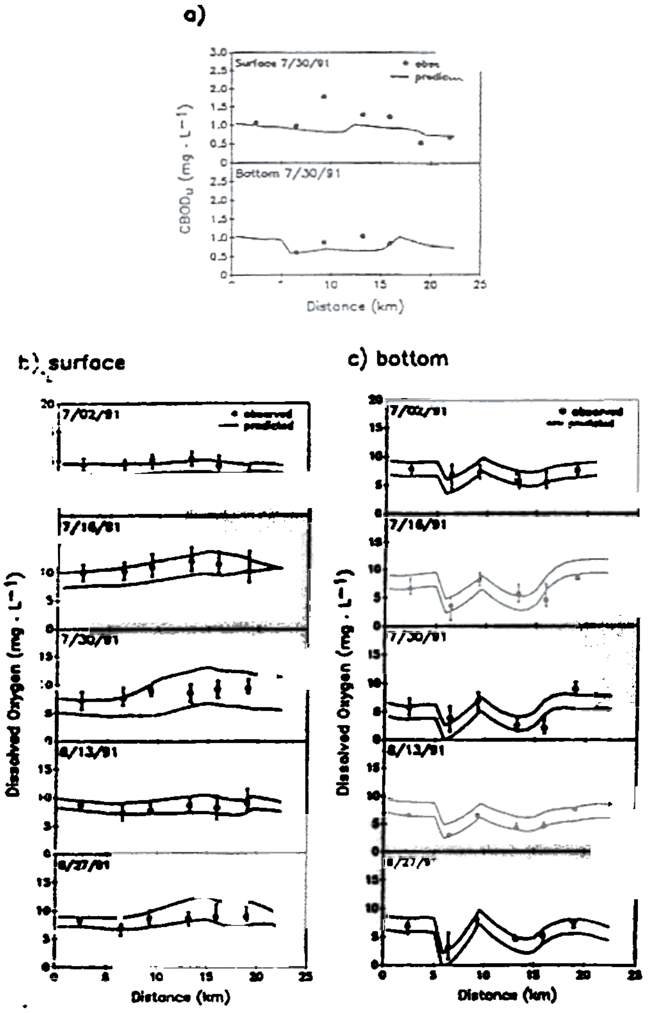


FIG. 5. Model Performance: (a) CBOD$_u$ Calibration; (b) Top Layer DO Validation; and (c) Bottom-Layer DO Validation

there was little structure in the distribution of CBOD$_u$ [e.g., Fig. 5(a)]. Precision of the CBOD$_u$ measurements is poor at the low concentrations that presently prevail in the river. The CBOD$_u$ submodel was calibrated to the observed distribution of CBOD$_u$ for the first diurnal survey ($k_c$ = 0.10 d$^{-1}$). Simulations of the calibrated CBOD$_u$ submodel matched the observed distributions of the other four diurnal surveys reasonably well [e.g., Fig. 5(a)].

Model performance for DO is presented for all five diurnal surveys for the upper and lower layers in Fig. 5(b and c), respectively. Simulations of daily average and diurnal values appear. The observed diurnals are equal to the dimensions of the bars, that reflect the range about the daily average. Daily average DO concentrations remain near saturation in the upper layer [Fig. 5(b)], offering little in the way of a test of the model. However, the unique depletions in the lower layer both upstream and downstream of the lake inflow [Fig. 5(c)], and the observed diurnal variations in both layers [Fig. 5(b and c)] offer good tests of model performance. The model performed well in simulating the upstream and downstream DO sags of the lower layer [Fig. 5(c)]. Further, the predictions of diurnal variations in the upper layer tracked the observations well for most of the surveys [Fig. 5(b)]. The diurnal variation of survey No. 3 was overpredicted, perhaps as a result of a nonuniform vertical distribution of phytoplankton in the upper waters (e.g., the volume-weighted concentration of chlorophyll may have been less than the near-surface concentration measured). The success of the upper-layer diurnal predictions support [illegible]lidity of the delta method that uses $k_a$ and $P_g$ (Chapra and [illegible]Toro 1991). The significant diurnal variations observed in the lower layer, beyond the depth of light penetration, reflects propagation from the upper layer, mediated by vertical mixing; as well as diurnal variation in the upper waters of Onondaga Lake discharged through the outlet to the river. Therefore the model uses the average of measured diurnal variations in the lower layer to calculate the range in concentration. This phenomenon is not directly accounted for in the model.

Calibration procedures were used in the transport submodel to determine components of the flow budget and mixing processes, and in the CBOD$_u$ submodel. However, the framework and coefficients of these submodels remained fixed in the modeling of DO. All other model inputs were established by measurements or the outcome of experiments. Thus, based on the high performance of the models for DO [Fig. 5(b and c)] for all five surveys, the water-quality model is considered validated and reliable for management applications.

## Analysis by Model

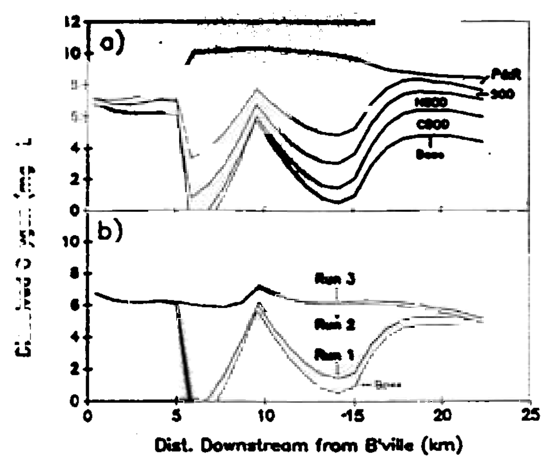


FIG. 6. Model Analyses for DO in Lower Layer of Seneca River: (a) Components of DO Depletion; (b) Projected Improvements for Scenarios (Run 1: Year-Round Nitrification at METRO with Stratification; Run 2: "Destratification"; Run 3: "Destratification" with Year-Round Nitrification at METRO)

observed for T-$NH_3$ concentrations in the lake outflow. Earlier, Effler et al. (1984) had attributed the DO depletions in the lower layer of the river largely to respiration and decay of phytoplankton released from Onondaga Lake.

Nitrification is the only sink of oxygen amenable to reduction, related to the Onondaga Lake inflow, without diverting a portion or all of the METRO discharge from the lake. Year-round nitrification at METRO would reduce the concentration of TKN in the upper waters of the lake to about 1.07 $mg \cdot L^{-1}$ thereby reducing the nitrogenous oxygen demand in the lower river layer. This reduction, that would only be achieved at great cost [about $200,000,000; Stearns & Wheler (1992)], would fall far short of eliminating the violations of the DO standard in the river [run 1, Fig. 6(b)]. The phytoplankton respiration component of the lower-layer depletion could be reduced by diverting the METRO discharge to the Seneca River downstream of the outlet. However, even at a much reduced concentration of Chl in the lake discharge (e.g., Chl = 10–20 $\mu g \cdot L^{-1}$, consistent with the diversion), violations of the DO standard may continue at critical low flow.

The dominant factor responsible for the contraventions of water-quality standards in the Seneca River adjoining the Onondaga Lake inflow is the reduced vertical mixing associated with the occurrence of chemical stratification. Elimination of this stratification [i.e., $E_v$ values observed upstream and downstream of the bounds of stratification, Fig. 3(g)] would eliminate the violations of the DO (and ammonia) standard presently observed [run 2, Fig. 6(b)]. This could be achieved by eliminating the ionic gradient between the lake and river, or artificially inducing turbulence in the river. Continuing industrial loads to the lake (Effler et al. 1991) are responsible for the lake's higher salt content (Doerr et al. 1994). However, it may not be practical to remediate this ionic pollution. Regardless of the means used to accomplish it, it is clear that "destratification" will be necessary to eliminate prevailing water-quality violations, and will be an integral component of any management plan aimed at remediating the water-quality problems of Onondaga Lake through diversion of the METRO load to the Seneca River. Year-round nitrification would result in only a minor increase in oxygen concentration beyond that achieved by "destratification" alone [run 3, Fig. 6(b)].

## SUMMARY

Comprehensive field monitoring and kinetic experimental programs were conducted to support the validation of the DO model. Further, a separate transport model was necessary to accommodate the hydrodynamic complexities of the system. Routine monitoring clearly documented the occurrence of chemical stratification and coupled violations of DO and $NH_3$ standards in the lower layer of the river adjoining the point of entry of the Onondaga Lake inflow during low-flow periods. Clear signatures of DO depletion adjoining the lake inflow, and diurnal variations along the entire study reach for five different surveys offered good tests of model performance for DO. The "tuning" process common to typical model-calibration efforts was minimized for this water-quality model by independently specifying the kinetic coefficients, based on the results of detailed experimental studies for the model coefficients. The salinity mass-balance framework of the transport submodel took advantage of the high salinity of the lake to resolve the complex hydrodynamic interplay between the river and the lake.

Validation of the DO model for the Seneca River has been demonstrated. Specifically, the model performed well in matching depletions in the lower layer of the river and diurnal DO variations. Model analyses indicated that the biochemical oxygen sinks of nitrification, sediment oxygen demand, and phytoplankton respiration all contribute significantly to the DO depletions observed in the lower layer of the river. Model projections have demonstrated that "destratification" of the river will be necessary to eliminate prevailing water-quality violations.

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## APPENDIX II. N[illegible]ON

*The following symbols are used in this paper:*

$C_i$ = concentration of DO is segment $i$ ($mg \cdot L^{-1}$);
$C_s$ = concentration of DO at saturation ($mg \cdot L^{-1}$);
$CBOD_u$ = concentration of ultimate CBOD ($mg \cdot L^{-1}$);
$Chl_i$ = concentration of chlorophyll in segment $i$ ($\mu g \cdot L^{-1}$);
COD = concentration of chemical oxygen demand ($mg \cdot L^{-1}$);
$H$ = river depth (m);
$H_l$ = river depth of lower layer (m);
$H_u$ = river depth of upper layer (m);
$I$ = irradiance ($\mu E \cdot m^{-2} \cdot s^{-1}$);
$J$ = T-$NH_3$ flux from sediment ($mg \cdot m^{-2} \cdot d^{-1}$);
$k_a$ = reaeration coefficient ($d^{-1}$);
$k_c$ = CBOD decay rate ($d^{-1}$);
$k_d$ = light-attenuation coefficient ($m^{-1}$);
$k_f$ = film-transfer coefficient for T-$NH_3$ at sediment-water interface ($m \cdot d^{-1}$);
$K_I$ = half-saturation coefficient for irradiance ($\mu E \cdot m^{-2} \cdot s^{-1}$);
$K_L$ = oxygen-transfer coefficient ($m \cdot d^{-1}$);
$k_n$ = NBOD decay rate ($d^{-1}$);
$K_p$ = half-saturation coefficient for SRP ($\mu g \cdot L^{-1}$);
$K_{SF}$ = $SF_6$ transfer coefficient ($m \cdot d^{-1}$);
$k_{x,T}$ = value of kinetic coefficient $x$ at temperature $T$ ($d^{-1}$);
$k_{x,20}$ = value of kinetic coefficient $x$ at 20°C ($d^{-1}$);
$NBOD_u$ = concentration of ultimate NBOD ($mg \cdot L^{-1}$);
$P_g$ = gross photosynthesis (mg $O_2 \cdot \mu g$ chlorophyll$^{-1} \cdot d^{-1}$);
$P_{g,max,20}$ = maximum chlorophyll-specific rate of gross photosynthesis (mg $O_2 \cdot \mu g$ chlorophyll$^{-1} \cdot d^{-1}$);
$P_n$ = chlorophyll-specific rate of net photosynthesis (mg $O_2 \cdot \mu g$ chlorophyll$^{-1} \cdot d^{-1}$);
$R$ = chlorophyll-specific plant respiration (mg $O_2 \cdot \mu g$ chlorophyll$^{-1} \cdot d^{-1}$);
$R_{20}$ = chlorophyll-specific respiration rate at 20°C (mg $O_2 \cdot \mu g$ chlorophyll$^{-1} \cdot d^{-1}$);
SRP = concentration of soluble reactive phosphorus ($\mu g \cdot L^{-1}$);
SOD = sediment oxygen demand (mg $O_2 \cdot m^{-2} \cdot d^{-1}$);
$T$ = temperature (°C);
$t$ = time (d);
$V_i$ = volume of model segment $i$ ($m^3$);
$\Theta$ = dimensionless temperature coefficient;
$\Theta_p$ = dimensionless temperature coefficient for photosynthesis; and
$\Theta_R$ = dimensionless temperature coefficient for respiration.